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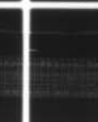
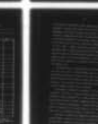
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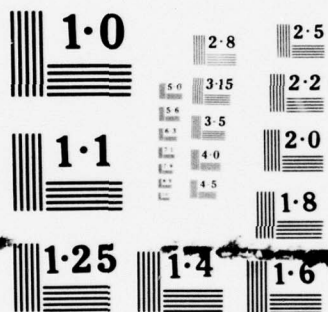
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IMPROVED FISHBITE ARMOR FOR DEEP-SEA
MOORING LINES

by

Bryce Prindle

WOODS HOLE OCEANOGRAPHIC INSTITUTION
Woods Hole, Massachusetts 02543

August 1977

TECHNICAL REPORT

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Earl E. Hays

Earl E. Hays, Chairman
Department of Ocean Engineering

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ABSTRACT

An improved procedure for the collection and correlation of deep-sea lines fishbite data with geographical location and ambient conditions is described. Triggerfish and a small shark, Isistius brasiliensis, are added to the list of suspected biters. The first known instance of fishbite on a deep-sea mooring line at a station moored in the Indian Ocean is recorded.

A screening test procedure for identification of thermoplastics which have a potential for use in protecting mooring lines against fishbite has been developed. Results of tests made on materials which are currently in production indicate that suitable materials may be found among the fluoropolymers, ABS resins, cellulose esters, acrylic/PVC alloys, polyterephthallates, and nylons. Five specific resins are recommended for trial on experimental deep-sea mooring lines.

Introduction

The nature of damage to deep-sea lines by biting marine organisms and the development of methods for controlling the same have been review in a previous publication, "Deep-Sea Lines Fishbite Manual" (Prindle and Walden, 1976).

Biting of lines was ascribed mainly to sharks and other fish, though the possibility that organisms, such as squid and sea turtles might occasionally cause damage remained a possibility. Available data indicated that biting occurred almost exclusively in deep-water locations beyond the continental shelf and in warm waters occupying a zone between approximately 40° north and 40° south latitudes. Bites were found at depths from the surface to 2000 meters below. Data used in reaching these conclusions were derived largely from stations moored in the western north Atlantic Ocean. More data are needed to complete the definition of the fishbite problem on a geographical basis.

After a study of various methods of solving the fishbite problem, it was concluded that armoring with a tough thermoplastic offered the most promise for protection of synthetic fiber lines and for lines carrying metallic conductors. Several experimental lines armored with thermoplastics; polyethylene, polycarbonate, rigid polyvinyl chloride, and acetal copolymer were made and tested at sea. Each had some favorable properties but none could be considered acceptable for routine use. It was evident that the field of commercially available materials would have to be systematically searched to find materials which had the toughness and environmental durability needed for the job.

In consideration of the foregoing, this report is in two parts. The first part supplements information given in the "Deep-Sea Lines Fishbite Manual" on the occurrence and nature of fishbite attack. The second is an account of a systematic search for improved thermoplastic armors.

Part I. Continued Collection of Fishbite Data

To facilitate collection and classification of significant information, a data storage card was devised to serve both as an aid in collecting fishbite data and for classification and filing of the same. Figure 1 is a copy of the data card which, by punching and sorting, can be used for retrieval and correlation of data as well as for storage. It is hoped that in time a sufficient sample of the facts relative to occurrence or non-occurrence of fishbite in various locations will be on file so that persons who plan the use of deep-sea moored stations can ascertain the hazard of fishbite for any part of the ocean.

Most of the new data collected since completion of the Deep-Sea Lines Fishbite Manual confirmed information already on record. However, there were several items which expanded the scope of the problem. Worthy of note among the new data are records of fishbite incidents from ocean areas other than the western north Atlantic, and the implication of types of biters not listed in the fishbite manual.

With reference to fishbite areas, an additional record of shark attack upon a mooring line in the Pacific Ocean has come to light (Sessions and Brown, 1969). A buoy line constructed of 14.3 mm (9/16") diameter nylon coated with polyurethane and located at 29°59.3' N latitude and 165°01.4' W longitude was severely bitten at a depth of 184 m. Shark tooth fragments were found embedded in the line at a depth of 210 m. Several electrical conductors were cut. Sessions and Brown's article indicates that another, similar line on station at 43°00.0' N latitude and 164°00.1' W longitude "had about half as many cuts and slashes". No tooth fragments were found in the latter case, but if the damage were indeed the result of biting it would be novel because it occurred outside the 40° north and south latitude zone suggested (Prindle and Walden, 1976) as the outer limits for such activity.

Figure 1

Deep-Sea Lines Fishbite Data

Please fill in data indicated below insofar as possible:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	
7	4	2	1	7	4	2	1	7	4	2	1	7	4	2	1	7	4	2	1	7	4	2	1	7	4	2	1	7	4	2	1	7	4	2	1
Name:																	Moored Station Identification:																		
Address:																																			
Float depth (m):																	Mooring line																		
Site: Lat.:																	Diameter:																		
Long.:																	Material:																		
Water depth (m):																	Armor:																		
Duration (days):																	Depth top (m):																		
Date in:																	Depth bot.(m):																		
Date out:																	Bites																		
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7	4	2	1	7	4	2	1	7	4	2	1	7	4	2	1	7	4	2	1	7	4	2	1	7	4	2	1	7	4	2	1	7	4	2	1
91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	

Additional information or comments:

The first authenticated record of fishbite in the Indian Ocean was obtained when the anchor line of Woods Hole Oceanographic Institution's Moored Station #593 was hauled from the water at 0°03' N latitude and 50°29' E longitude. The line was a steel cable, 4.76 mm(3/16") diameter, coated with high density polyethylene to an outside diameter of 6.91 mm (0.272"). Slashes and stabs were found in the polyethylene jacket at a depth of 1411 m. The underlying wire was exposed at several locations. Two fish tooth points were found in the plastic, but they were too small for further identification.

Among possible new species of biters are triggerfish and the "cigar" or "cookie cutter" shark, Isistius brasiliensis. More information is needed concerning their possible roles in damage to deep-sea mooring lines.

Part II Improved Fishbite Armor

The need for fishbite armor on deep-sea mooring lines has been described in the "Deep-Sea Lines Fishbite Manual"(Prindle and Walden, 1976). Several plastics have been used for the purpose. The most widely applied have been polyethylene and polyurethane. They are both readily available and easily applied. However, study of lines returned from service indicates that a tougher material to prevent penetration of fish teeth to tensile fibers and/or electrical conductors within the mooring lines is needed.

First attempts at finding improved armor were to apply materials which were readily available and seemed to have sufficient toughness to lengths of line, and then, to test the jacketed lines by using them as component parts of deep-sea moored stations. Polycarbonate, rigid polyvinyl chloride, and acetal copolymer have all been tested in this way. Each has been found to have its particular shortcoming. Polycarbonate was destroyed by stress crazing. Rigid PVC broke up when handled on deck at winter temperatures. Acetal copolymer was notch sensitive, so its use was limited to one mooring because nicks produced by fish teeth led to later cracking when the line

was flexed. The outcome of such tests was valuable in pointing up characteristics which would be necessary in a good armor, but the method of testing at sea was very slow and expensive, requiring up to nine months time for each plastic tested and the use of oceanographic vessels.

According to one handbook (Howard, M. J., 1977) there are presently available something in the order of "50 major chemical types and 175 subgroups of moldable and extrudable plastics". More than 4000 individual kinds of plastics are available from 137 manufacturers. Amongst such a wealth of material, there may be an ideal fishbite armor. The problem is to find the right plastic quickly and efficiently. A screening test procedure is obviously needed.

The purpose of the study reported herein is twofold:

- a. Development of a screening test procedure for preliminary selection of resins which have the potential of becoming effective mooring line armors, and
- b. A review and testing of commercially available materials to find plastics which will qualify for sea trials in full scale mooring arrays.

A. Development of Screening Test Procedure

Test Specimens

In the first stages of plastic armor development (Prindle and Walden, 1976) tubes 13 mm ($\frac{1}{2}$ " ID with a wall thickness of 1.78 mm (70 mils) were used as test specimens for determining the resistance of plastics to cutting and stabbing. Such specimens had the advantage of being about the same size and shape as the armor on mooring lines in use at the time, and they were produced by extrusion so that they might be expected to have physical properties similar to those of an extruded armor. However, they are not a standard test item in the plastics industry and so it was found that many resins were not available for testing in the tube form.

The first step in devising a screening test procedure was therefore to see whether flex bars and tensile bars having a rectangular cross section, 3.175 mm (1/8") by 12.7 mm (1/2"), and which are widely used in the plastics industry, could be used instead of tubes.

The stab test (Prindle and Walden, 1976) was run on a series of four plastics which were available in both tube and bar form.

In the course of testing, it was found that some materials were so tough that the tips of sharks' teeth used in the stab tester were broken during the test procedure. This meant that a constant supply of new shark teeth had to be kept on hand; an impractical consideration. Therefore, all data herein reported were derived with the use of steel teeth which had been filed to approximate the size and shape of a tooth from a white tip shark.

Stab tests run on bars of plastic yielded higher values than those run on tubes, as illustrated by the following results:

Stab Test
Tubes vs Bars as Test Specimens

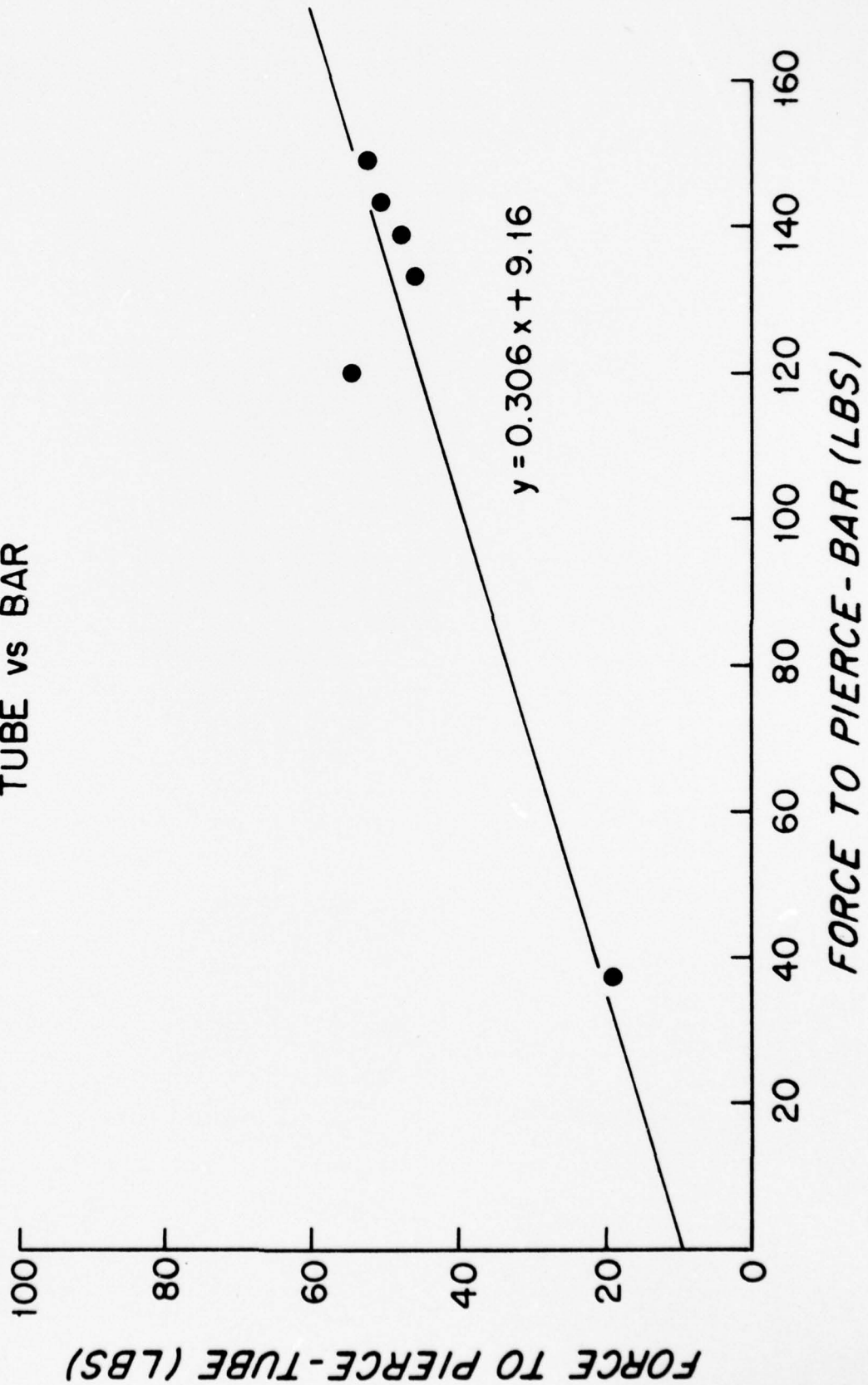
Items	<u>Stabbing force to pierce - lbs.</u>	
	<u>Tube</u>	<u>Bar</u>
Polyethylene	19	37
Polycarbonate	53	149
Acetal copolymer	53	120
Nylon 6/6	48	139

Data from tests on bars have a wider dispersion than those from tubes as seen in Figure 2. Although there are not enough data to establish precisely the degree of correlation between results obtained with the two types of tests, they appear to follow the same trend and it was decided to use stab tests on flex bars or tensile bars as a rough guide to the "biteability" of various plastics.

Figure 2

STEEL TOOTH STAB TEST

TUBE vs BAR



In similar vein, the cut test which had been done previously on tubes, was revised to use bars. In order to do so, it was necessary to change the specimen holder and the angle of the cutting blade in the test equipment (Prindle and Walden, 1976, p.62). The specimen holder was simply machined so that a specimen 3.18 mm by 12.7 mm ($1/8 \times \frac{1}{2}$ ") in cross section would be held with its broadside horizontally beneath the cutting blade.

The angle of the cutting blade was changed in order to obtain a draw cut, which is characteristic of fish teeth during a bite. With the cylindrical specimens previously used, a blade moving straight downward with its cutting edge horizontal produced a draw cut because of the curved surface of the test specimen. However, with a flat specimen, it became necessary to change the angle of the blade in order to get a draw cut. The angle was set at 45° to the horizontal. Numerical cut test values obtained with the new technique are lower than those previously obtained by about 15 to 20%. Otherwise, results obtained with various plastics appear to indicate the same relative resistance to cutting as had been determined using tubes as test specimens.

Durometer D Test

The cutting and stabbing tests as devised and used at Woods Hole were attempts to simulate the kinds of attack which mooring lines would encounter in service. They are not generally used in the plastics industry. An attempt was made therefore to see whether a test which is more widely used could be related to these specialized procedures and so facilitate the selection of candidate armor materials. The Durometer test using the shore D scale appeared to be suitable.

To determine whether there might be a useful correlation, cut, stab, and Durometer D tests were run on a series of resins in the form of flex bars or tensile bars (hereinafter called simply "test bars") having a cross section of 3.18 x 12.7 mm ($1/8 \times \frac{1}{2}$ "). Each test was run on the same test

bar of each plastic at room conditions, which were about 21°C (70° F) and a low relative humidity. Data are given in Table I in the Appendix.

It was evident that Durometer D measurements followed the same trend as cut and stab test data. In order to visualize the relationship, data were plotted against a regression line for the same, established by the method of least squares. Figure 3 shows the relationship between cutting force and Durometer D measurements; Figure 4, the relationship between stabbing force and Durometer D measurements. In both cases, the Durometer numbers cover a narrower range than the numerical values of the other variables, but there appears to be a strong correlation. If one does not set the limits too rigidly, it seems that the Durometer can be used as a method for preliminary screening of plastics for bite resistance.

Armor Specification

Sufficient experience has accumulated so that a tentative fish-bite armor specification can be set up in language familiar to suppliers of plastic resins. Major considerations are:

- a. Resistance to biting.
- b. Extrudability onto other mooring line components.
- c. Handleability.
- d. Environmental resistance.

Many of the requirements have been discussed and defined (Prindle and Walden, 1976). No material tested to date has possessed all properties to an ideal degree, but as progress has been made from one experimental armor to the next, a picture of the desired resin has begun to emerge. It must be more cut-resistant than polyethylene; less brittle than rigid PVC; not subject to stress cracking like polycarbonate; and more resistant to cracking when notched than is acetal copolymer. Figure 5 is a tentative specification in outline form showing the test parameters which are though to be significant, based upon experience with armored lines to date.

Figure 3

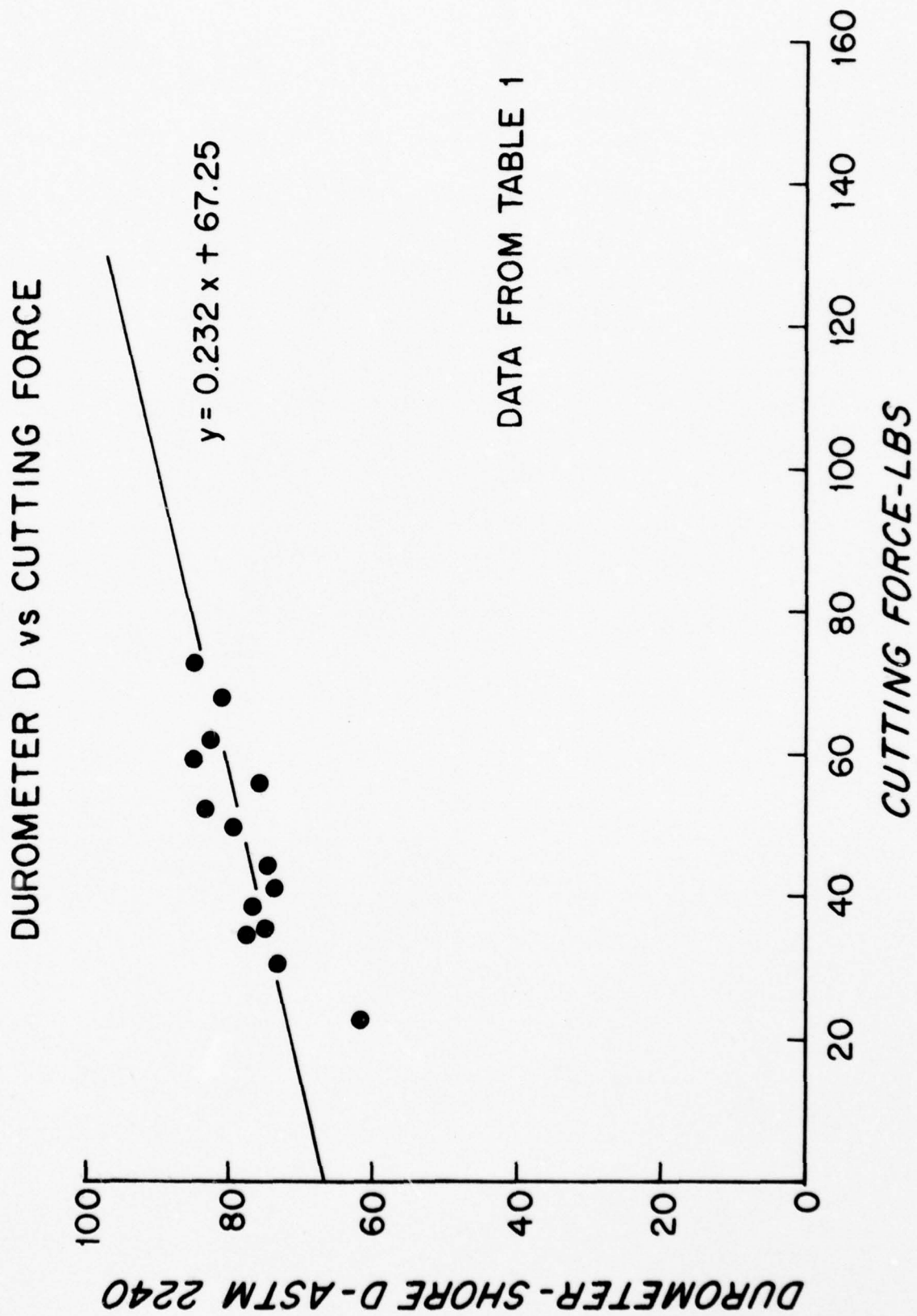
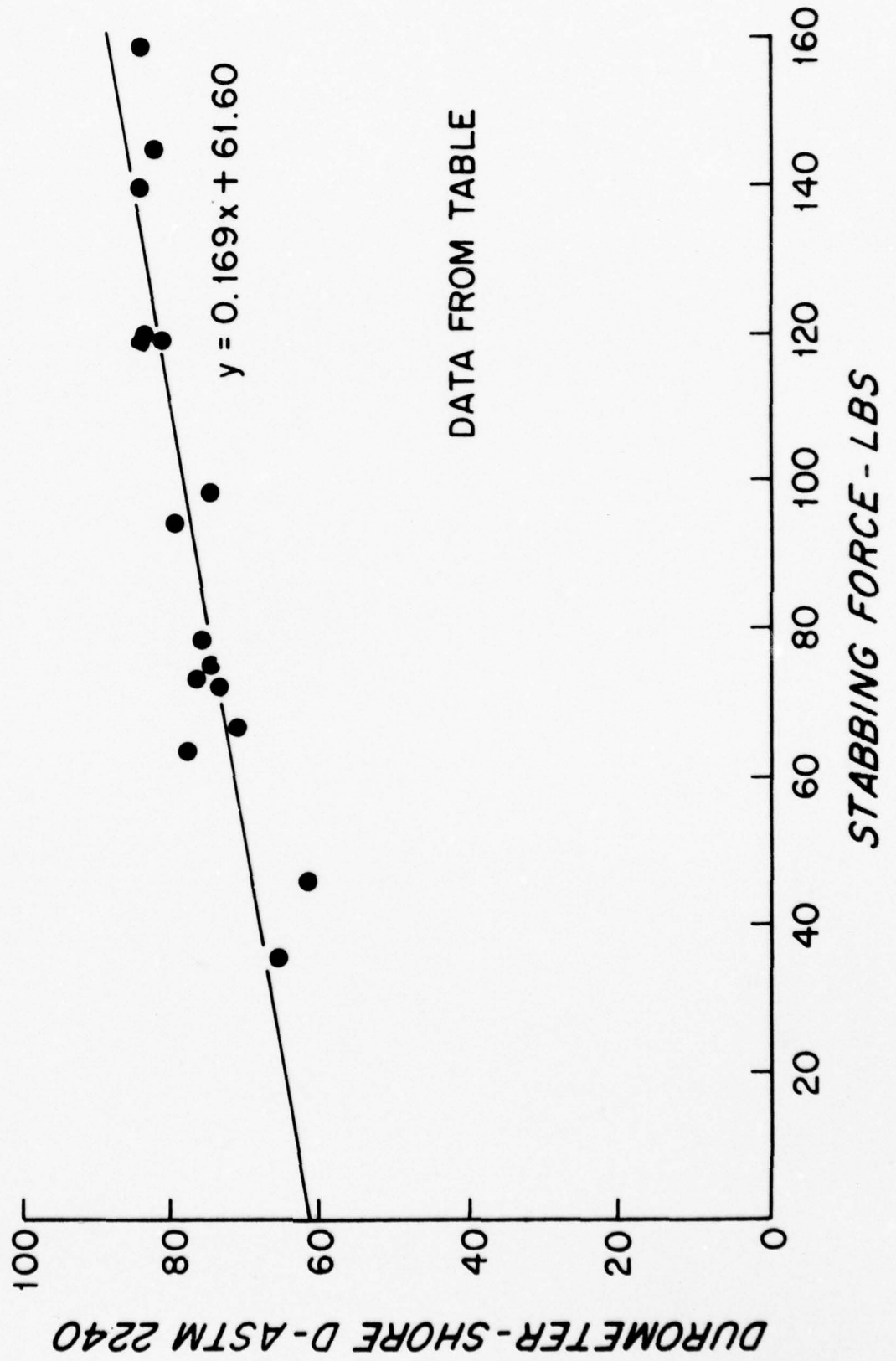


Figure 4

DUROMETER D vs STABBING FORCE



The specification outlined in Figure 5 was designed as an aid in screening plastics for possible use as fishbite armor. It does not take into consideration all the information one should have before using a material on a line which is to be part of a deep-sea mooring. In addition, it would be desirable to determine the properties of a candidate armor when saturated with water; to learn more of the effects of low temperature on its physical properties; and of course, to ascertain the probability of success in extruding it onto rope. A material which passes the Tentative Specification and then performs well under these latter considerations should then be ready for test on a mooring line at sea.

In using the Tentative Specification, it should be understood that the requirements as listed represent what is thought to be an ideal armor. If all the limits were met, the material would be no more dense than sea water, exceedingly tough, easily extruded, and unaffected by the environment. As a practical matter, some compromise with these standards is a likely necessity. It is important, therefore, to note the priority of items listed in the specification.

Toughness is obviously the prime requirement. If a material does not meet the limits indicated under "TOUGHNESS" it may either have insufficient resistance to biting or be too brittle for use under some conditions.

Specific gravity is a low priority item. From an ideal standpoint, armor should not add to the weight of a line in sea water. A tendency to float might even be helpful. An armor with low density will cost less for a given length of line than another with high density at the same cost per unit weight. However, in terms of utility specific gravity is not a limiting factor for most thermoplastics.

Thermal properties are critical. Extrusion temperature and other properties, such as melt viscosity, determine whether a thermoplastic can

Figure 5
Candidate Armor Material (tentative specification)

Trade Name: _____ Generic Name: _____

Source: _____

Properties	Test	Units	Requirement	Data
<u>TOUGHNESS</u>				
Cutting force	DSLFM 62*	lbs	35+	
Stab resistance				
Durometer Shore	ASTM 2240	D scale	75+	
Steel tooth	DSLFM 62	lbs	70+	
Impact;notched Izod	ASTM D256	ft lbs/in	2+	
Tensile modulus	ASTM D638	lbs/in ² x 10 ⁵	3+	
Brittleness temp	ASTM D746	°F	0-	
Elongation to break	ASTM D638	%	10+	
<u>SPECIFIC GRAVITY</u>	ASTM D792		1.025-	
<u>THERMAL PROPERTIES</u>				
Extrusion temperature		°F		
Use range		°F	0 to 120	
<u>STIFFNESS</u>				
Flexural modulus	ASTM D790	lbs/in ² x 10 ⁵	4.0-	
<u>ENVIRONMENTAL RESISTANCE</u>				
Stress cracking			Excellent	
Hydrolysis			Excellent	
Sun and oxidation			Excellent	
<u>CLARITY</u>			Transparent	

REMARKS:

DSLFM 62 = Deep-Sea Lines Fishbite Manual, page 62
DSLFM 62* - Same as DSLFM 62 but cutting angle modified to 45°. See p. 8 this report.

be successfully extruded onto tensile fibers and/or conductors. More experience is needed before limits can be set, but in general, low extrusion temperatures and low melt viscosity favor success. Equally important is the range of temperature over which an armor material can be used without failing from brittleness on the one hand or plastic flow on the other. In the water, deep-sea lines are subjected to temperatures from -2°C to 27°C (29 to 80°F). However, they may be required to perform under a much wider range of temperatures when stored or handled on deck or on shore. Difficulties have been experienced when armored lines were run over small diameter sheaves at low winter temperatures. Minus 18°C to $+49^{\circ}\text{C}$ (0°F to $+120^{\circ}\text{F}$) has been suggested as a practical range for most applications in the temperate zone.

Stiffness places a constraint upon line handling, but tough materials are likely to be stiff. A flexural modulus limit of 4.0×10^5 lbs/in² has been found acceptable for 1.78 mm (70 mil) thick armor on a 12.7 mm ($\frac{1}{2}$ ") diameter Dacron line of low twist, parallel yarn construction. This is obviously a critical factor, but one which may need adjustment as larger or smaller diameter mooring lines are employed.

Environmental resistance is necessary if a line is to be used repeatedly. Resistance to stress crazing is essential. Polycarbonate possesses excellent properties in all other respects but it cannot be used because minute amounts of organic compounds present in synthetic fiber ropes cause it to break up spontaneously. Hydrolysis and other effects due to water are significant in a material which is to be used for long periods under water at considerable pressure, as noted later in this report.

Resistance to sunlight and oxidation are important if lines are stored outdoors, uncovered, or the end of a mooring line is secured above the water line. Beyond the first meter of submergence in sea water, amounts of ultraviolet radiation from the sun have been reduced by more than 90%

(von Arx, 1962) and it seems unlikely that a significant rate of degradation would take place from that cause. The resistance of many plastics to ultraviolet radiation can be greatly increased by the incorporation of carbon black or other materials, and this seems a well advised precaution. Ratings given in Table II are for unprotected resins.

B. Review and Testing of Commercially Available Thermoplastics

Upon the basis of the Tentative Specification which had been developed, the field of available plastics was searched for armor materials, using the 1975-76 Modern Plastics Encyclopedia (Agranoff, 1976) as a prime reference. About 15 different kinds of plastic resins seemed to have potentially useful properties.

Information was collected together with test bars in order to evaluate the various materials against the specification. Technical data from manufacturers was used wherever available. Cut, stab, and most Durometer tests were done at the Woods Hole Oceanographic Institution. The tests were run in a heated building with test bars conditioned to ambient conditions. Outdoor temperatures were below 0° C (32° F) so relative humidity inside the laboratory was low.

As information accumulated, it began to appear that the best armor materials would be types used in other applications requiring toughness; uses such as bearings, golf ball covers, trim strips, and of course, cable jacketing. Several of the resins which seemed to have the right properties had been used in injection molding. Because of high melting points of such materials and their high viscosity when melted, it is anticipated that some will be on the borderline for extrusion onto rope. Estimated material cost varied widely from a low of \$37/500 m of armored line to a high of \$555/500 m of line, not always in proportion to value as armor.

Data for four plastics which have been tested at deep-sea moored

stations and for eleven new materials are given in Table II in the Appendix. Data for each resin are given in comparison to the limits set by the Tentative Specification. Data for four previously tested plastics have been included for comparison with those which are new.

Few of the candidate armor materials meet all of the specified requirements. One might rate them on a scale as follows:

A - Meet all specification requirements:

Fluoropolymer E-CTFE

A(?) - May finally rate "A" but a few items of data are not yet available.

Polyphenylene oxide

Polyterephthallate (80-20) and (60-40)

Cellulose butyrate

B - Generally acceptable, but a few properties are borderline or a little below specification. May be useful compromises.

Acrylic/PVC alloy

Acrylonitrile-Butadiene-Styrene

Nylon

C - Materials which have properties below specification, but which are easily applied, give some protection, and may be considered where fishbite is not a major problem.

Polypropylene

Ionomer

Polyurethane

After preliminary screening, six new resin formulations which seemed to be most promising were further tested to determine the effect of water immersion upon resistance to cutting and stabbing. Specimens were tested for Durometer D hardness, resistance to cutting, and resistance to stabbing after 24 hours in distilled water at room temperature (approx. 21°C) and a

pressure of one atmosphere. The same tests were repeated after 15 days under the same conditions. Another set of specimens of the same plastics was tested in the same manner after 24 hours under water at room temperature and 205 atmospheres pressure (3000 psi, corresponding to hydrostatic pressure at a depth of 2000 meters in sea water). Data from the tests are given in Table III in the Appendix. The same data translated into terms of percent of the value obtained for a dry specimen are shown graphically in Figures 6, 7 and 8.

From the bar graphs, it appears that immersion in water did not change the resistance of the polyterephthallates or of the acrylic/PVC specimens to a significant degree. In some cases, resistance to cutting and stabbing seemed to have increased during water immersion. However, in view of the variability of available data and the small number of replicate tests, (3), it is doubtful that such apparent gains in resistance to mechanical "biting" are significant. 7

On the other hand, cellulose butyrate and nylon seem to have suffered significant and progressive loss of resistance to cutting and stabbing during immersion in water.

Such a change could have been anticipated in the case of nylon which is known to absorb water and change its physical properties. The absorbed water apparently has a plasticizing effect on the nylon, causing it to become softer and more easily cut. At the same time, however, its notch sensitivity declines. In the case of the nylon tested, Zytel ST801, the changes in cut and stab resistance are enough to put it below specification levels. A tougher nylon, such as nylon 6, Capron 8207, might have enough excess bite resistance to make it useful even when saturated with water.

Cellulose butyrate seems also to have been adversely affected by immersion in water in a way similar to nylon.

Figure 6

Effect of Water Immersion
of
Durometer D Hardness

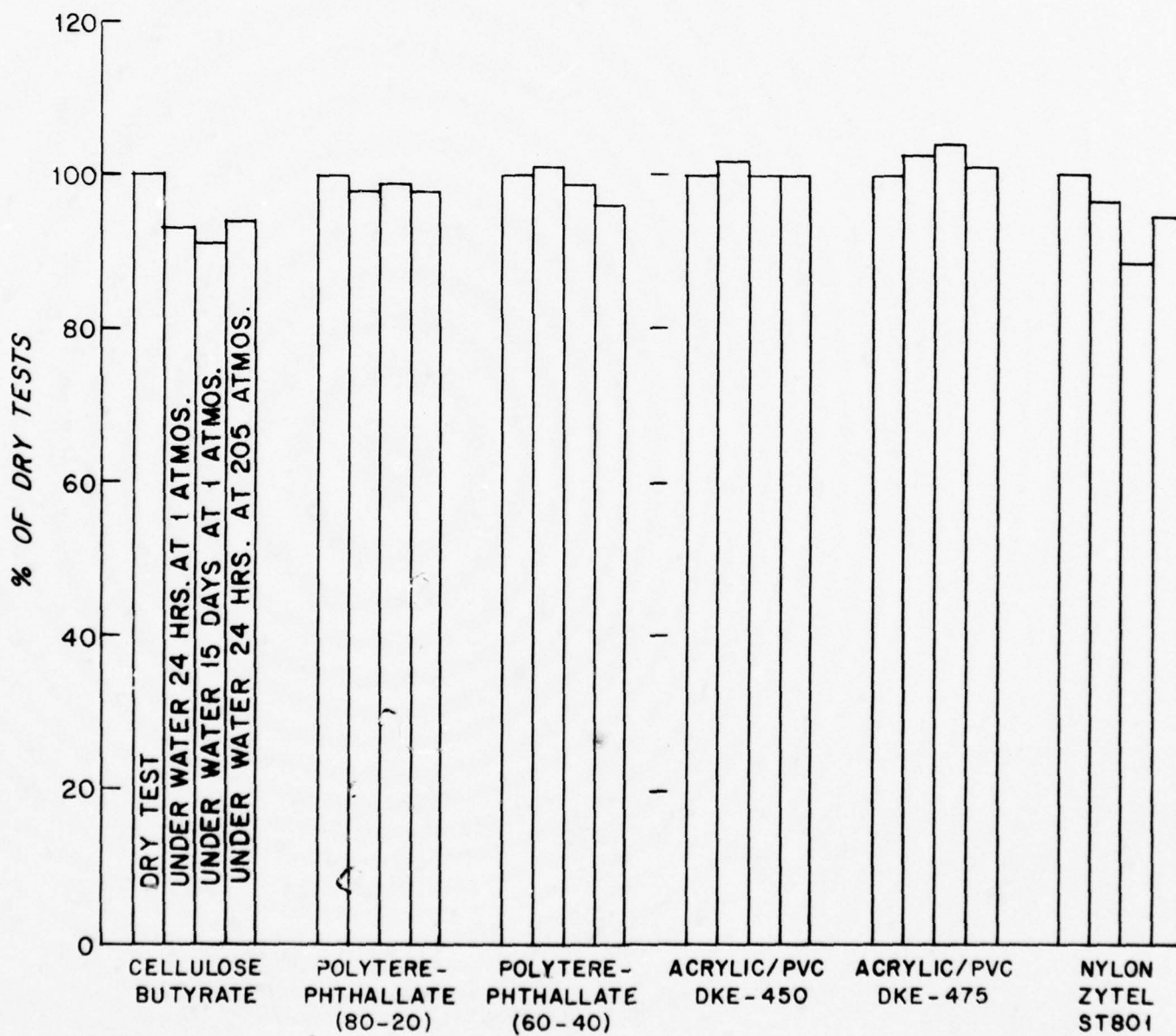


Figure 7

Effect of Water Immersion
on
Resistance to Stabbing

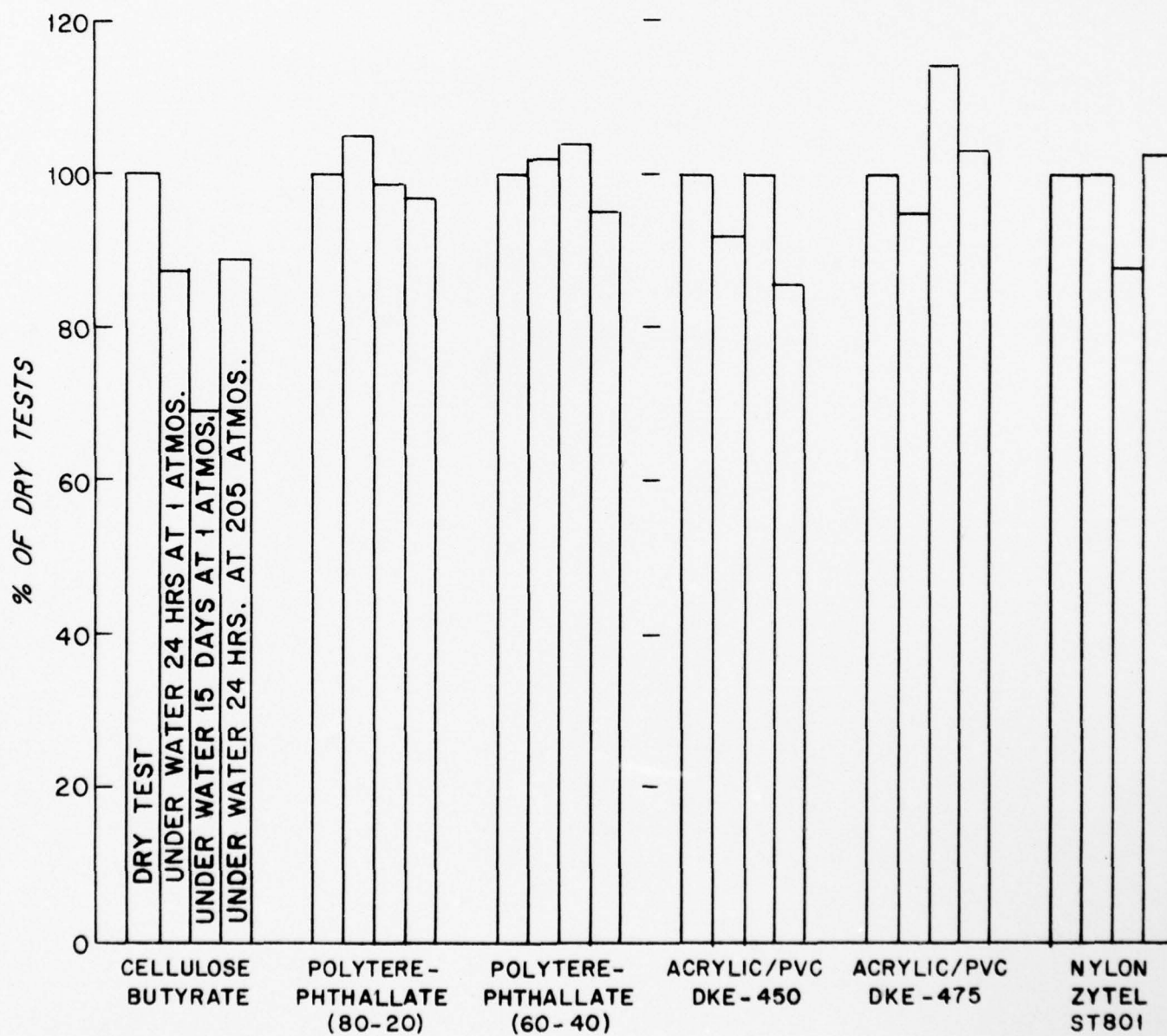
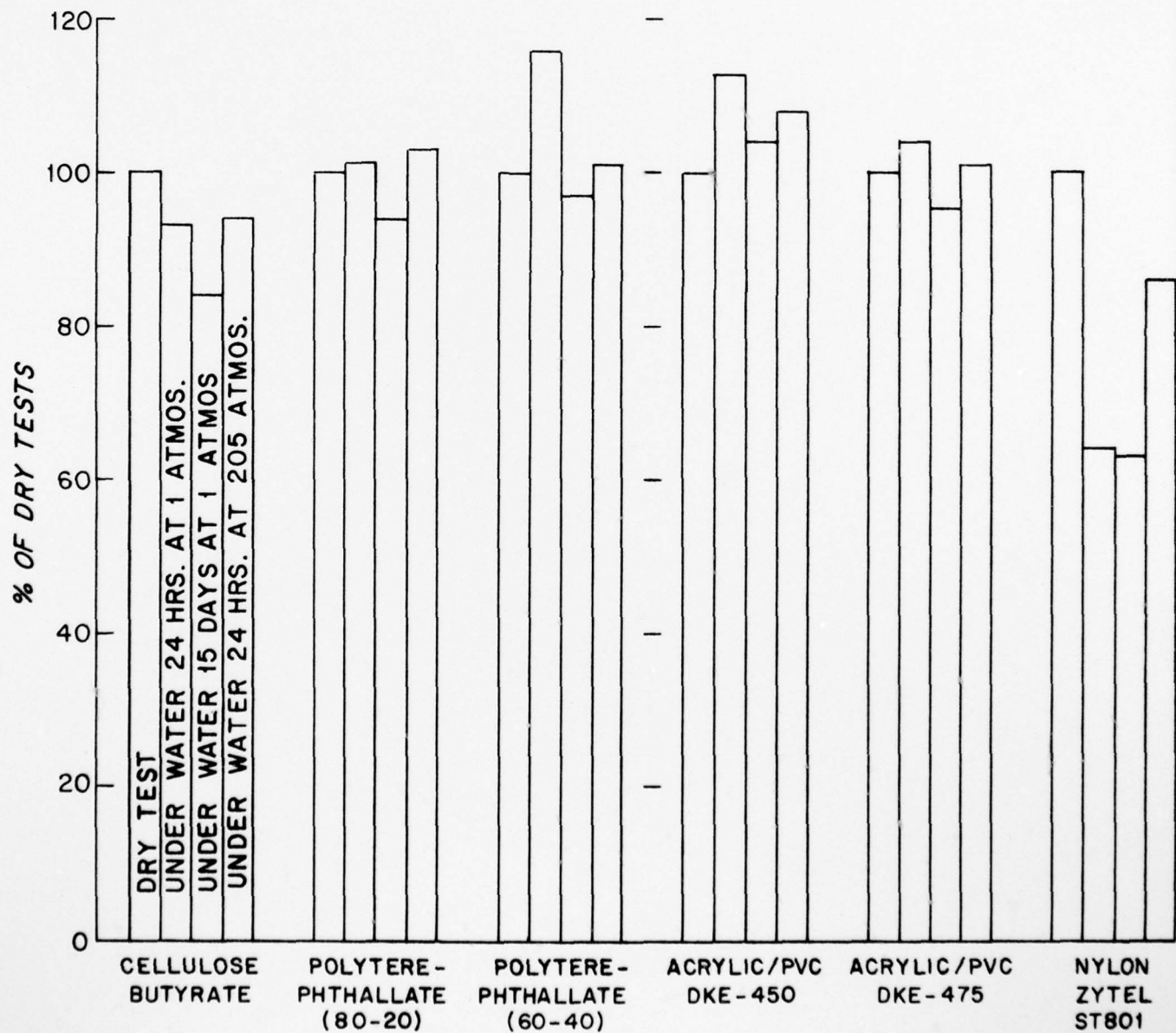


Figure 8

Effect of Water Immersion
on
Resistance to Cutting



Increasing hydrostatic pressure from one atmosphere to 205 atmospheres for a period of 24 hours did not result in more rapid loss of cut and stab resistance by any of the plastics.

As a result of the screening test program, eleven commercially available thermoplastics which have suitable properties have been found. Five of them satisfy the requirements of a Tentative Specification to a degree that they are ready for a trial on an experimental mooring line at sea. They are:

1 & 2. Acrylic/PVC - "DKE 450" and "DKE 475"

Source: E. I. duPont de Nemours and Co.
Plastic Products and Resin Dept.
Experimental Station Building
Wilmington, Delaware 19898

Contact: Mr. William E. Garrison
Research Associate

DKE 450 and DKE 475 are inexpensive materials. Both have been used in extrusion. DKE 450 is a little tougher than DKE 475 and has better properties at low temperatures. On the other hand, DKE 475 is more resistant to sunlight and is less stiff.

3. Acrylonitrile - butadiene - styrene (ABS) - "Kralastic SR-S 1801"

Source: Technical Services
Uniroyal Chemical
Elm Street
Naugatuck, Connecticut 06770

Contact: Dr. Jerry Klender

Kralastic SR-S 1801 has been used successfully in marine applications.

4. Fluoroplastic E-CTFE - "Halar 300"

Source: Specialty Chemicals Division
P.O. Box 1087R
Norristown, New Jersey 07960

Contact: Mr. A. Bruce Robertson

This material has excellent properties and has been extruded onto wire. It should make a long lasting product, but it is very expensive.

5. Fluoroplastic - "Tefzel 280"

Source: Plastics Department
E. I. duPont de Nemours and Co.
Wilmington, Delaware 19898

Contact: Dr. John O. Punderson

This material has excellent properties. It has been successfully extruded. Some corrosion resistant extruder parts are necessary, as it gives off minute amounts of hydrofluoric acid during extrusion. It is very expensive, but should make a long lasting product.

* * * * *

There are several materials which look promising for use as mooring line armor, but they need a small amount more preliminary evaluation and/or testing before recommendation for sea trial. They are:

Cellulose butyrate - "Tenite butyrate 205A - 37201 MH"

Source: Plastics Division
Eastman Chemical Products Inc.
Building 280
P.O. Box 431
Kingsport, Tennessee 37662

Contact: Mr. Kenneth L. Gibson

Properties when immersed in water need further testing with reference to cut and stab resistance and brittleness at low temperature.

Nylon - "Capron 8207"

Source: Allied Chemical
Specialty Chemicals Division
P.O. Box 1087R
Morristown, New Jersey 07960

Contact: Mr. E. C. Lupton

- "Zytel ST 801"

Source: E. I. duPont de Nemours and Company
Plastic Products and Resin Department
Technical Service Laboratory
Chestnut Run
Wilmington, Delaware 19898

Contact: Dr. Robert M. Bonner

Nylons are marginal with reference to bite resistance, but have high elongation and low stiffness. They absorb water and are plasticized thereby becoming less sensitive to cracking. They need further evaluation in the wet condition.

Polyterephthallate - "Polyterephthallate + XEP-16-1"
(80-20 and 60-40)

Source: Plastics Division
Eastman Chemical Products, Inc.
Building 280
P.O. Box 431
Kingsport, Tennessee 37662

Contact: Mr. Kenneth L. Gibson

This is a new class of thermoplastics which is characterized by toughness and which can be blended to produce a wide range of properties. To date, the polyterephthallates look promising, but more data are needed with reference to thermal properties and environmental resistance.

* * * * *

A material which should be reconsidered:

Polyphenylene oxide - "Noryl"

Source: General Electric Co.
Plastics Department
Noryl Avenue
Selkirk, New York 12158

Contact: Mr. Morris M. Lee

A trial extrusion of Noryl SE-100 onto a Dacron line resulted in an unsatisfactory product because suitable extrusion facilities were not available at the time and the resin was degraded in process. However,

the physical properties of polyphenylene oxide still appear to be right for armor and improved forms of the polymer have become available recently so that a reconsideration is recommended.

Recommendations

1. It is recommended that armored lines be prepared for deep-sea mooring test from each of the five following thermoplastics: acrylic/PVC (DKE 450), acrylic/PVC (DKE 475), ABS resin (Kralastic SR-S 1801), fluoroplastic E-CTFE (Halar 300), and fluoroplastic (Tefzel 280). All have met screening test requirements and seem to have a potential for making good armors. (As a beginning, arrangements have been made for a trial extrusion of acrylic/PVC (DKE 450) onto a Kevlar line).
2. Evaluation of cellulose butyrate (Tenite butyrate), nylon 6 (Capron 8207), super-tough nylon (Zytel 801), and polyterephthallates should be completed and mooring lines made if results continue to be favorable.
3. Evaluation of phenylene oxide polymers (Noryl) should be re-opened with consideration given to new types of polyphenylene ethers.
4. Access to information concerning commercially available thermoplastics has been greatly improved within the past few months, and a review of the field would be in order if a satisfactory armor does not result from application of those already studied.
5. If a variety of resins are to be applied as armor, an extrusion facility capable of handling them with a minimum of retooling should be found.

APPENDIX

Table I
Cut, Stab, and Durometer Data
for
Various Armor Candidate Materials

Generic Name	Trade Name	Cutting Force Lbs.	Stabbing Force Lbs.	Durometer Shore D
Acetal copolymer	Celcon M25-04	52	120	84
Acrylic/PVC alloy	DKE 450	62	147	83
Acrylic/PVC alloy	DKE 475	68	119	82
Acrylonitrile-butadiene-styrene (ABS)	Kralastic SR-S 1801	39	73	77
Cellulose butyrate	Tenite butyrate*	50	94	80
Fluoropolymer E-CTFE	Halar 300	56	79	76
Fluoropolymer	Tefzel 280	41	72	74
Ionomer	Surlyn 1801	23	46	62
Nylon	Capron 8207	59	139	85
Nylon	Zytel ST 801	35	63	78
Polycarbonate	Lexan 101-111	73	149	85
Polyethylene	Super Dylan 5900	17	37	66
Polyphenylene oxide	Noryl SE 100	57	119	84
Polyterephthallate	6P50 + EP-16-1(80-20)	45	98	75
Polyterephthallate	6P50 + EP-16-1(60-40)	36	75	75
Specification	**205A-3720 1 MH	35+	70+	75+

TABLE II

ARMOR CANDIDATE MATERIALS

Test	Units	Tentative Specification									
<u>THERMOPLASTIC</u>											
Generic Name			Acetal copolymer	Acrylic/PVC Alloy	Acrylic/PVC alloy	Acrylonitrile-Butadiene-Styrene	Cellulose butyrate	Fluorocarbon E-CTFE	Fluorocarbon	Ionomer	
Trade Name			Daloon M25-04	DKE 450	DKE 475	Kralastic SR-61801	Tenite 205A37201M	Nalar 300	Tefzel 180	Sullyn 1801	
Source			Celanese	duPont	duPont	Uni-Royal	Eastman	Allied Chemical	duPont	duPont	
<u>TOUGHNESS</u>											
Cutting force	DLFPH 62*	lbs.	35+	52	62	68	39	50	56	41	23
Stab resistance											
Durometer	ASTM 2240	D scale	75+	84	83	82	77	80	76	74	62
Steel tooth	DLFPH 61	lbs.	70+	120	147	119	73	94	74	72	46
Impact; notched Izod	ASTM D256	ft lbs/in	2+	1.6	12.0	18.2	7.5	5.7	No break	No break	
Tensile modulus	ASTM D638	lbs/in ² x 10 ⁵	3+	4.1	3.7		3.1	2.0	2.4	1.2	
Brittleness temp.	ASTM D746	°F.	0-							-150	-166
Elongation to break	ASTM D638	%	10+	75	75 - 150	113		40	200	200	427
SPECIFIC GRAVITY	ASTM D792		1.025-	1.41	1.26	1.32	1.04	1.20	1.68	1.70	0.96
<u>THERMAL PROPERTIES</u>											
Extrusion temperature		°F.		360 - 400	410	410	400 - 440	257 - 347	450 - 540	572	400 - 500
Use range		°F.		0 to 120	- 120				0 - 120	0 - 120	0 - 120
<u>STIFFNESS</u>											
Flexural modulus	ASTM D790	lbs/in ² x 10 ⁵	4.0-	3.75	3.8	3.3	2.3	2.0	2.4	2.0	0.38
<u>ENVIRONMENTAL RESISTANCE</u>											
Stress crazing			Excellent	Very good	Good	Good			Excellent	Very good	Good
Hydrolysis			Excellent	Very good	Excellent	Good	Excellent		Excellent	Excellent	
Sun and oxidation			Excellent	Good	Poor	Good	Poor		Excellent	Excellent	

DLFPH = Deep-Sea Lines Fishbite Manual, page 62

DLFPH 62* - Same as DLFPH 62 but cutting angle changed to 45°. See p. 8 this report.

MATERIALS

		Acrylonitrile-Butadiene-Styrene	Cellulose Butyrate	Fluorocarbon E-CTFE	Fluorocarbon	Ionomer	Nylon 6	Nylon	Polyphenylene Oxide	Polycarbonate	Polyethylene, high density	Poly-terephthalate	Poly-terephthalate
0/PVC Alloy	Acrylic/PVC alloy												
0	DKE 475	Kralastic SR-61801	Tenite 205A17201M	Malar 300	Tefzel 280	Burlin 1801	Capron 8207	Zytel ST801	Noryl SE-100	Lexan 101-111	Super Dylan 5900	GP50 + KEP-16-1 (80 - 20)	GP50 + KEP-16-1 (60 - 40)
	duPont	Uni-Royal	Eastman	Allied Chemical	duPont	duPont	Allied Chemical	duPont	General Electric	General Electric	ARCO/Polymers	Eastman	Eastman
62	68	39	50	56	41	23	59	35	57	71	17	45	36
83	82	77	80	76	74	62	85	78	84	85	66	79	75
47	119	73	94	79	72	46	139	63	119	149	37	98	75
12.0	18.2	7.5	5.7	No break	No break		4.0	15	5.0	16	5.0	2.0	3.8
3.7		3.1	2.0	2.4	1.2			2.1	3.8	3.45			
					-150	-166					-100		
150	113		40	200	200	427	300	40	50	110	700	290	390
1.26	1.32	1.04	1.20	1.68	1.70	0.96	1.13	1.09	1.10	1.20	0.96		
10	410	400 - 440	257 - 347	450 - 540	572	400 - 500			400 - 450				
120				0 - 120	0 - 120	0 - 120	0 - 120	0 - 120	-40 - 300		0 - 120		
1.8	3.3	2.3	2.0	2.4	2.0	0.38	1.4	2.55	3.6	3.2 - 3.5	0.8	2.08	1.41
Good	Good			Excellent	Very good	Good		Excellent		Very poor	Excellent		
Excellent	Good	Excellent		Excellent	Excellent		Excellent	Good	Excellent	Good	Excellent		
Poor	Good	Poor		Excellent	Excellent		Poor	Poor	Good	Good	Poor		

Table III

Effect of Water Immersion
on Resistance of Plastics to Penetration

Material	Dry Test	Wet Test		
		Immersed in Distilled Water		
		1 Atm. 24 hrs.	1 Atm. 15 days	205 Atm. 24 hrs.
	Durometer	D - Ave. 5		
Cellulose butyrate	79.6	74.2	73.0	75.0
Polyterephthallate 80-20	79.0	77.8	78.2	77.4
Polyterephthallate 60-40	75.1	76.0	74.6	71.8
Acrylic/PVC (DKE 450)	82.9	84.4	83.0	82.8
Acrylic/PVC (DKE 475)	81.9	84.6	85.0	82.6
Nylon (Zytel ST801)	77.9	75.4	69.2	74.0
Specification	75			
Stab Test - Lbs. - Ave. 3				
Cellulose butyrate	94.3	82.3	65.0	84.2
Polyterephthallate 80-20	97.7	102	97.0	95.0
Polyterephthallate 60-40	75.1	76.3	78.5	71.0
Acrylic/PVC (DKE 450)	145	134	145	124
Acrylic/PVC (DKE 475)	119	114	136	123
Nylon (Zytel ST801)	62.4	62.2	55.2	64.6
Specification	70+			
Cut Test - Lbs. - Ave. 3				
Cellulose butyrate	50.3	46.8	42.5	47.3
Polyterephthallate 80-20	44.8	45.3	42.3	46.3
Polyterephthallate 60-40	35.8	41.5	34.7	36.2
Acrylic/PVC (DKE 450)	61.8	69.7	64.5	66.5
Acrylic/PVC (DKE 475)	69.0	71.7	65.2	69.8
Nylon (Zytel ST801)	40.3	25.9	25.2	34.8
Specification	35+			

Table IV

Effect of Water Immersion
on "Bite" Resistance of Armor Materials

Material	Dry Test	*Wet Test - % of Dry		
		1 Atm. 24 hrs.	1 Atm. 15 days	204 Atm. 24 hrs.
	Durometer D - Ave. 5			
Cellulose butyrate	79.6	93	92	94
Polyterephthallate 80-20	79.0	98	99	98
Polyterephthallate 60-40	75.1	101	99	96
Acrylic/PVC (DKE 450)	82.9	102	100	100
Acrylic/PVC (DKE 475)	81.9	103	104	101
Nylon (Zytel ST801)	77.9	97	89	95
	Stab Test - lbs. - Ave. 3			
Cellulose butyrate	94.3	87	69	89
Polyterephthallate 80-20	97.7	104	99	97
Polyterephthallate 60-40	75.1	102	105	95
Acrylic/PVC (DKE 450)	145	92	100	86
Acrylic/PVC (DKE 475)	119	96	114	103
Nylon (Zytel ST801)	62.4	100	88	103
	Cut Test - lbs. - Ave. 3			
Cellulose butyrate	50.3	93	84	94
Polyterephthallate 80-20	44.8	101	94	103
Polyterephthallate 60-40	35.8	116	97	101
Acrylic/PVC (DKE 450)	61.8	113	104	108
Acrylic/PVC (DKE 475)				
Nylon (Zytel ST801)	40.3	64	63	86
Specification				

*Immersed in distilled water.

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<p>WOODS HOLE OCEANOGRAPHIC INSTITUTION WHOI-77-54</p> <p>IMPROVED FISHBITE ARMOR FOR DEEP-SEA MOORING LINES by Bryce Prindle. 33 pages. August 1977. Prepared for the Office of Naval Research under Contract N00014-76-C-0197; NR 083-400 and the National Data Buoy Office of the National Oceanic and Atmospheric Administration under Contract H83609A.</p> <p>An improved procedure for the collection and correlation of deep-sea lines fishbite data with geographical location and ambient conditions is described. Triggerfish and a small shark, <i>Isistius brasiliensis</i>, are added to the list of suspected biters. The first known instance of fishbite on a deep-sea mooring line at a station moored in the Indian Ocean is recorded.</p> <p>A screening test procedure for identification of thermoplastics which have a potential for use in protecting mooring lines against fishbite has been developed. 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